SOLUBILITY

IN THE

VAPOUR PHASE.

by

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INTRODUCTION.

It was first observed by Hannay and Hogarth that a solution of a salt in a liquid on heating above the critical temperature of the solution does not necessarily deposit the dissolved salt on the disappearance of the liquid phase. They showed for example, (Chem. News, 1880, 41, 103.) that a solution of potassium iodide in ethyl alcohol could be heated to a temperature of about 100° C above the critical temperature of the solution without any deposition of the salt.

Pictet, (Compt. rend. 1895, 78, 26.) heated solutions of borneol, cineol and terpineol in ether to temperatures above the critical temperature without any deposition of the solute.

P. Villard, (Chem. News, 1898, 78, 297.) found that easily volatile solids like iodine and camphor will dissolve to an appreciable extent even at ordinary temperatures in compressed gases such as oxygen and methane.

In 1898 Dewar (Proc. Chem. Soc. 14, 241.) observed that the colour of iodine vapour was less dense in a vacuous flask than in one at the same temperature containing air and that the colour in the latter was more purple than in the former. It was suggested that this increase in colour was due to a greater volatility of the iodine in air than in vacuum.

Centnerszwer and Tetelow (Zeit. Electrochem. 1903, 9, 799.) have made some interesting experiments on the solution of anthraquinone in liquid sulphur dioxide. They found that if a certain quantity of anthraquinone is heated in a sealed tube with a definite quantity of sulphur dioxide the following phenomena occur.

1st. The liquid expands and then diminishes in volume owing to evaporation until all the liquid disappears at temperature t_1

2nd. As the temperature rises further the quantity of anthraquinone left undissolved diminishes and then liquid reappears at temperature t_2

3rd. The solid anthraquinone passes entirely into the liquid sulphur dioxide at temperature t_3

4th. The liquid phase finally disappears at temperature t_4

Obviously from the above the solubility of anthraquinone increases with rise of temperature.

Tyrer (J.C.S. 1910, 621.) makes the very interesting statement that solubility in the vapour phase is a function of the concentration of the solvent. The extension of this idea to the liquid phase would explain the rather sudden decrease in solubility in the liquid phase just before the critical temperature. He further claims that the solubility in the vapour phase decreases with rise in temperature although the solvent concentration remains the same and further that the decrease is greater for the greater concentrations of the solvent. This would suggest the formation of unstable compounds, like hydrates, which dissociate under the influence of heat.

E.P. Bartlett (J. Am. Chem. Soc. 1927, 49.) as a result of extensive work on the water content of ammonia synthesis gases has come to the following conclusions.

1st. The actual water vapour content of a saturated gas is larger than is calculated by the usual method in which temperature effects are alone considered and the volume is calculated by means of the laws of a perfect gas. The amount of water

vapour increased with the pressure but not in proportion to the increase in density of the gas.

2nd. The magnitude of the phenomena depends on the nature of the gas, nitrogen holding 44% more water vapour than the same volume of hydrogen at 1000 atmospheres and 50°C. This difference is not due or explained by a difference of free space in the gas. The amount of water vapour taken up by a 3:1 hydrogen : nitrogen mixture could have been interpolated using the rule of additive volumes (Leduc) at constant temperature and pressure.

EXPERIMENTAL.

All the iodine used in these experiments was obtained by sublimation. A mixture of 3 parts iodine and 1 part potassium iodide was heated and the sublimed iodine collected on a cold clean glass surface.

In the first instance the experiments of Dewar were repeated. Iodine was sealed in a vacuous bulb and heated in water to 90°C. The depth of colour was noted and the tip of the bulb

broken. With the inrush of air the colour of the vapour at once deepened very considerably and became more purple. This was repeated using a bulb of known volume and containing less iodine than would saturate the available space with vapour at the temperature of the experiment. On allowing the air to enter the same effect was again observed. However in this case, since no excess of iodine was present this colour change cannot be attributed to the increased volatility of iodine in air as was suggested by Dewar.

A qualitative spectroscopic examination of this effect was undertaken. A small quantity of iodine was placed in a Lilburn flask which was then evacuated to a pressure of about 1 mm. by means of a Sprengel mercury pump, and then sealed off. The sealed flask was held concentrically in a large beaker of water placed in front of the slit of a Hilger photographic spectroscope. The water was maintained at 90°C during the experiments. A beam of light from a Point - o - lite lamp was used as the source of illumination.. Comparative photographs were then taken on a panchromatic plate, first with the iodine alone in the vacuous bulb and then, at the same temperature, in the presence of air. Between these exposures the flask had been

removed from the beaker and when completely cold the tip had been carefully broken. The flask was then resealed and returned to the beaker, the utmost care being taken to ensure that the flask occupied the same position as before. When the temperature of the heating water had become perfectly steady again the second exposure was made. The results showed a considerable widening of the absorption band when air was present. Along with this increase in absorption the head of the band had also moved from the green towards the red end of the spectrum. The same effect entirely was observed when less iodine was used than would saturate the available space with vapour at the temperature of the experiment. A further series of photographs was then taken in experiments wherein the air was replaced successively by nitrogen, oxygen, carbon dioxide and argon. In all these experiments the identical result was obtained. In order to obtain a more accurate comparison of the effect of these gases, a small amount of iodine was placed in a 20 cm. polarimeter tube fitted with two side tubes. This was then placed in a glass - sided thermostat maintained at 50°C and arranged in front of the photographic spectroscope. A series of four photographs was then taken in which the gas

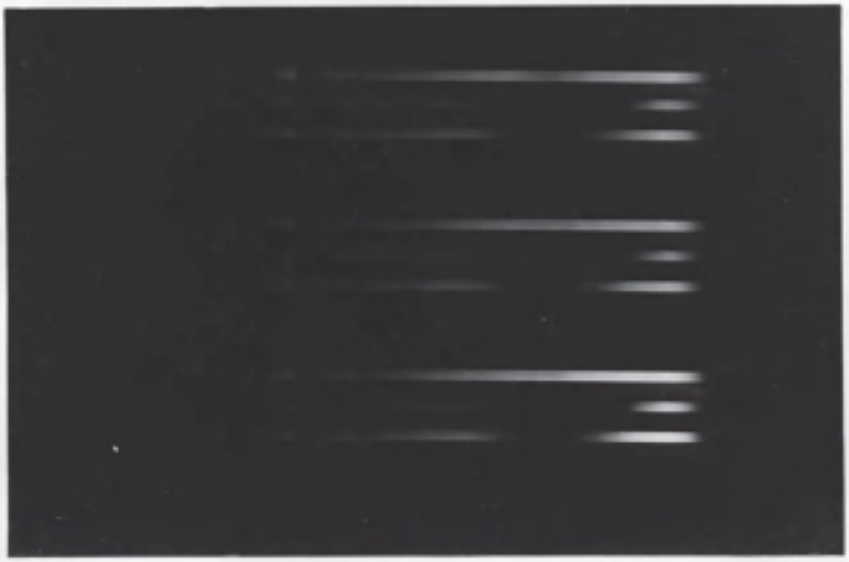


Plate 1.

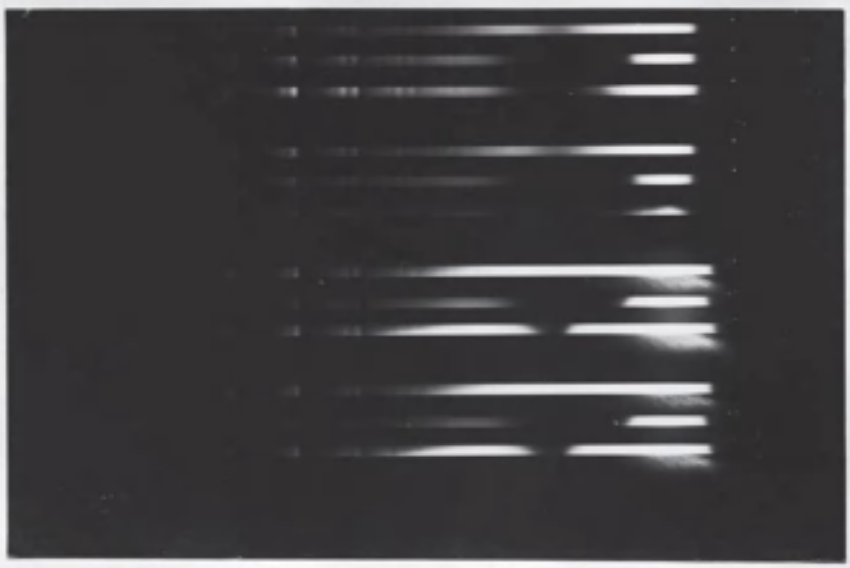
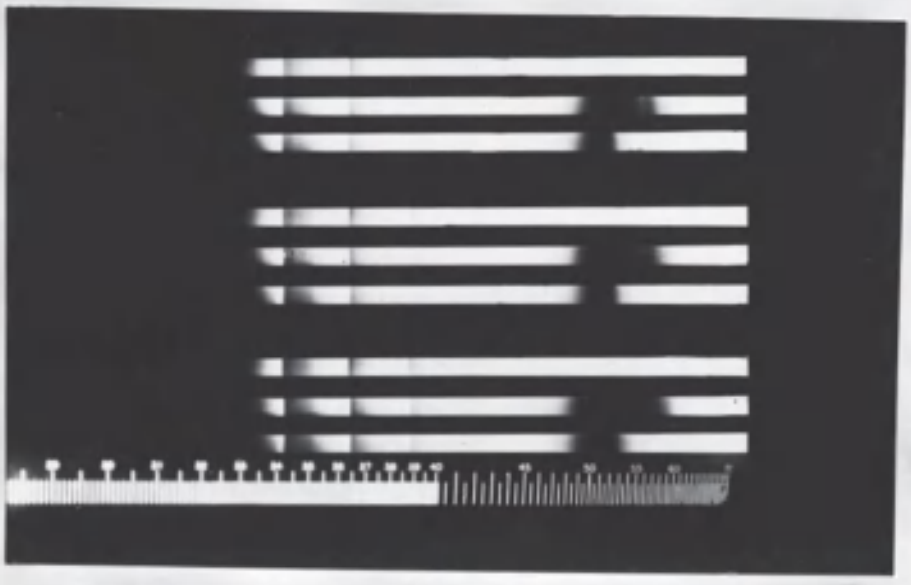


Plate 2.

Plate 3.



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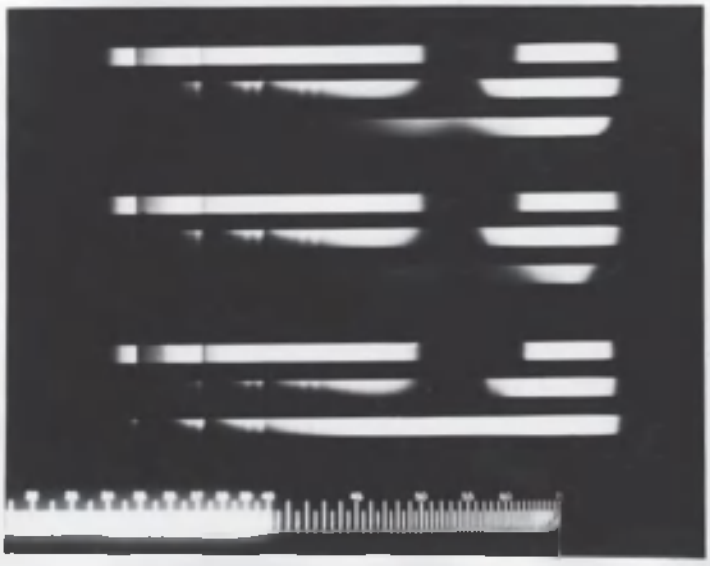

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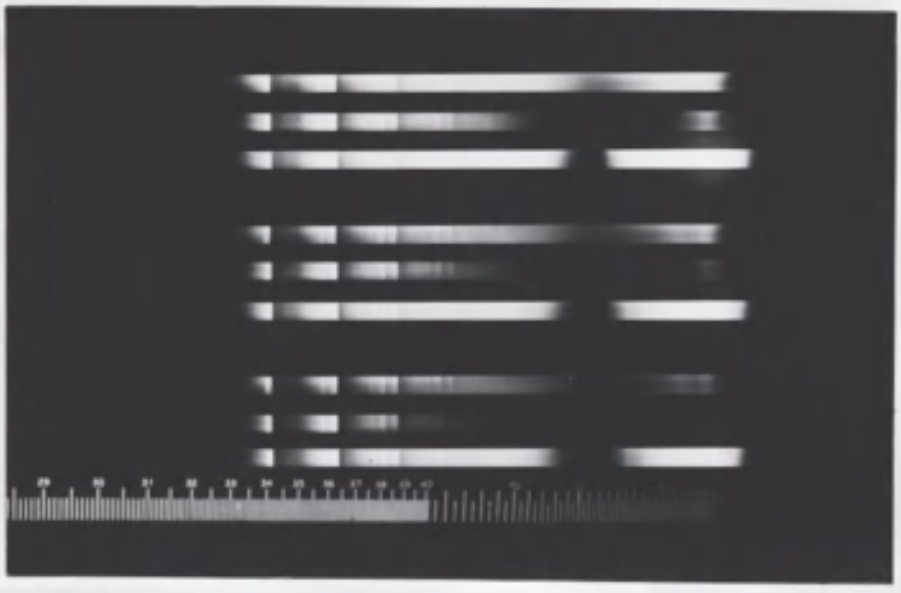


Plate 6.

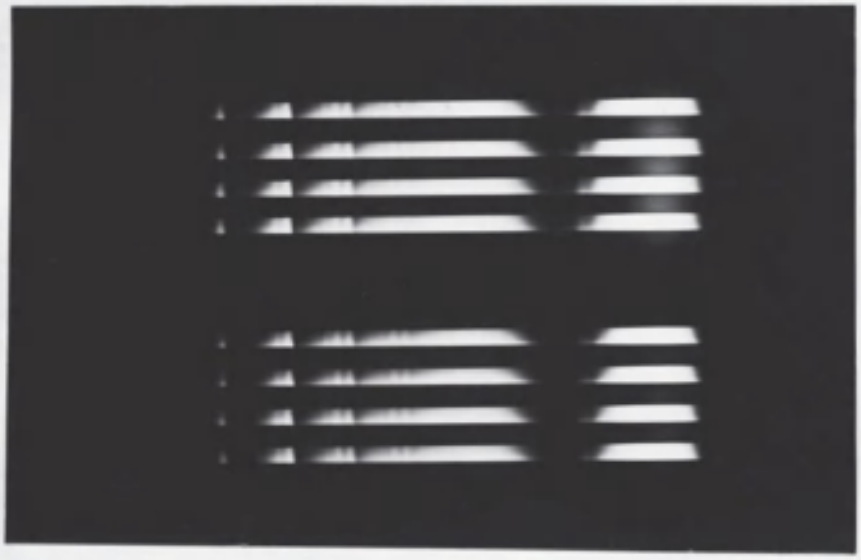


Plate 7.

in the tube was successively air, nitrogen, oxygen and carbon dioxide. In all four cases the spectra were identical.

In the accompanying photographs, Plate1 shows three sets (with different exposures, 30, 60, and 90 seconds) of iodine absorption spectra in air and in a vacuum, with a comparison continuous spectrum in each case. In this case considerably more iodine was used than would fill the available space with vapour at the temperature of the experiment. Plate2 shows three similar sets in air obtained when using less iodine than would saturate the available space with vapour. Plate3 shows three similar sets in nitrogen and in a vacuum, Plate4 in oxygen and in vacuum, Plate5 in carbon dioxide and in vacuum,and Plate6 in argon and in vacuum. Plate7 shows two sets of spectra of iodine taken in the 20 cm. polarimeter tube in presence of the four gases; air, nitrogen, oxygen and carbon dioxide.

Attempts were next made to determine quantitatively the amounts of iodine which would volatilise into a definite volume containing air and then into the same volume when vacuous. Various types of diffusion experiments were tried. For the most part these experiments consisted of allowing iodine, contained in the neck of the flask,

to diffuse into the flask. The iodine was retained in the neck of the flask by means of a pad of glass wool. After the iodine had been inserted the flask was carefully sealed off. In the first of these experiments narrow-necked flasks were used. The flasks were heated in a steam bath. In the case of the narrow-necked flasks the heating was continued for approximately nine hours. Wide- necked flasks were then tried. With this type of flask the heating period was decreased to six or seven hours. An attempt was also made using an evacuated flask and also an evacuated flask containing a little benzene. The following is the type of result obtained.

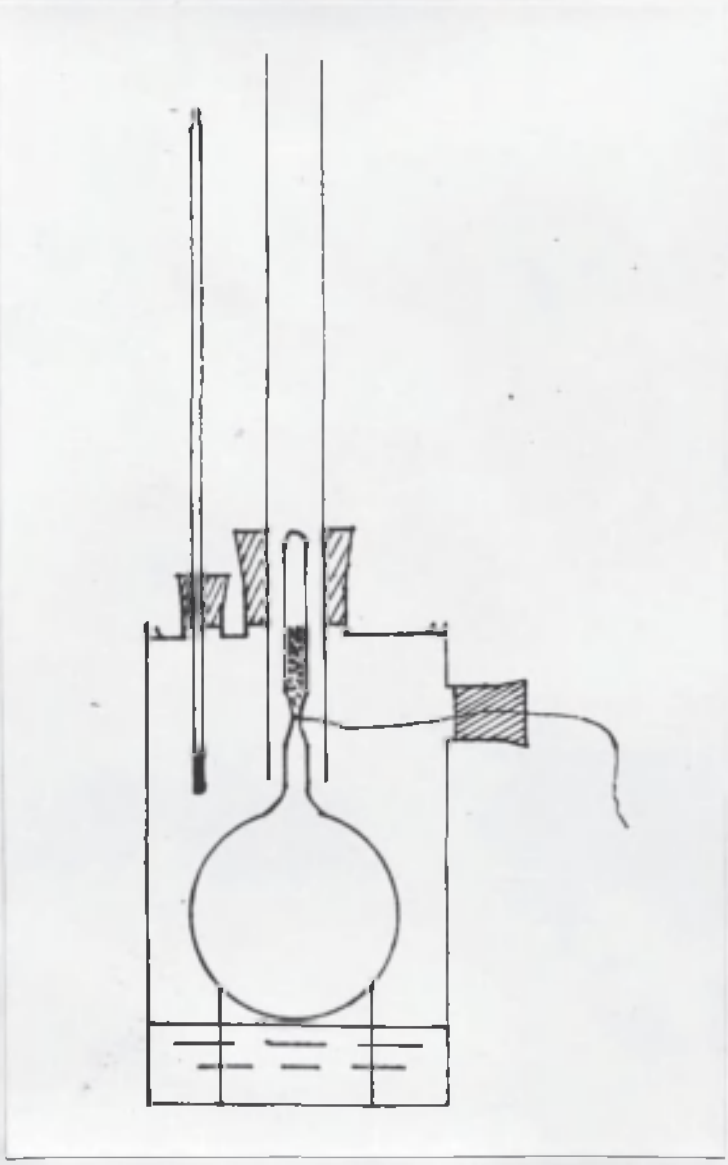
Iodine per 100cc. air at 100°C = (1)0.0515 gm.
(2)0.0586 gm.
(3)0.0424 gm.

Average = 0.0508 gm. Iodine.

Iodine per 100cc. vacuum at 100°C =0.0492 gm.

Iodine per 100cc. benzene vapour at 100°C
= 0.0568 gm.

These results would seem to indicate that it is possible to obtain different quantities of iodine diffusing into equal volumes containing different atmospheres. However they definitely



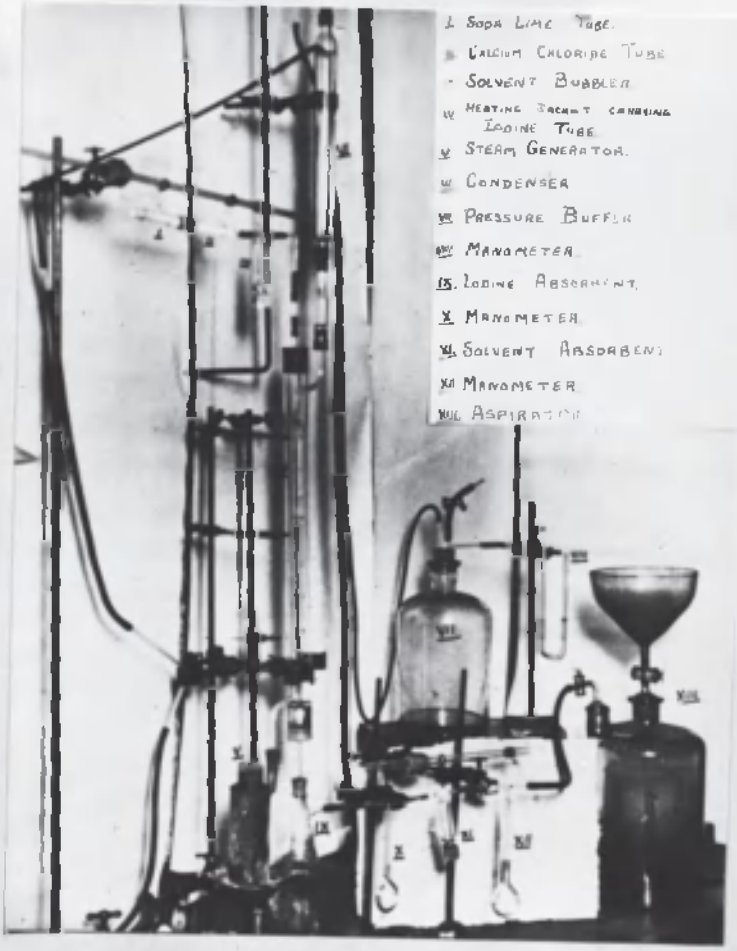
showed that the experiment is very sensitive to temperature changes; there is a decided parallel between the amount of iodine required to saturate a given volume of air and the atmospheric pressure, the higher the pressure the greater the amount of iodine diffusing. Thus it is seen to be essential that in all these experiments the temperature must be maintained constant. To obtain this a large 10 litre aspirator bottle, fitted with a manometer, was attached to the condenser, fitted to the steam bath, by means of pressure tubing. By increasing or decreasing the pressure in the aspirator, according as the atmospheric pressure is less than or greater than 760 mm., water can always be made to boil at 100oC.

About 0.5 gm. of iodine was placed in a flask of 130cc. capacity, the flask was sealed off, and while still hot the iodine was shaken into the neck where it melted and adhered to the glass close to the sealed tip. (Under favourable conditions only a very small quantity of iodine will sublime into the flask, but if this amount is excessive it may be driven back by a continued heating of the bulb and cooling of the neck.) The flask is now placed in the steam bath shown in Figure 1 and heated to 100°C. The steam bath was

constructed from a large lever-lidded paint tin fitted with a thermometer and a long brass tube to act as an air condenser, the upper end of the tube being atteched to the aspirator described above. After 5 - 7 hours heating the flask was removed from the bath and cooled as quickly as possible in a stream of water; the iodine vapour condensed on the walls and, since diffusion of the vapour in air is slow, during the cooling practically no iodine sublimed from the solid in the neck of the flask. The flask was now cut open, the amount of iodine in the flask determined by titration with N/50 sodium thiosulphate, and the volume of the flask determined by filling with water. For three consecutive experiments the quantity of iodine in 100 cc. was found to be practically constant.

When the same method was used with iodine in a vacuous flask the results obtained were much higher and were not constant. This was due to the sublimation of the iodine from the neck into the bulb which was cooling rapidly during the removal of the flask from the bath. Various attempts were made to avoid this and the most satisfactory result was obtained by breaking the neck of the flask while still in the bath, so that all sublimation

due to the quicker cooling of the bulb was avoided. For this purpose a slight modification of the method was necessary. The neck of the flask was made of 5 mm. tube and a constriction was made about 3 cm. from the bulb; 3 cm. above this constriction there was a plug of glass wool, on the top of this was placed the iodine in small pieces. The apparatus was now evacuated and sealed off. A loop of string was fastened to the constriction and the flask placed in position in the heater. The end of the brass condenser tube was pushed well down over the neck of the flask past the constriction. The string passed through a slot in the end of the brass tube and then through a stopper in the wall of the heater. A period of two hours heating was usually sufficient for the evacuated flask. The string was then pulled strongly drawing the neck of the flask against the condenser tube until the former fractured. Steam entered the bulb and the broken end fell into the water of the heating bath. The bulb was now removed from the heater and its iodine content and volume determined as before. The results for three consecutive estimations are shown in comparison with those obtained for air. They are not quite so regular but are always higher. The values for the vapour pressure of iodine are inserted in the table and are calculated on the


I. Soda Lime Tube.
II. Calcium Chloride Tube
III. Solvent Bubbler
IV. Heating Jacket containing Iodine Tube
V. Steam Generator.
VI. Condenser
VII. Pressure Buffer
VIII. Manometer
IX. Iodine Absorbent
X. Manometer
XI. Solvent Absorbent
XII. Manometer
XIII. Aspirator

assumption that iodine vapour obeys the gas laws and the gram-molecular volume is 22.4 litres at N. T. P.

Weight (gm.) of saturated iodine vapour in 100cc. at 100°C

	a.	b.	c.
In air.....	0.05032	0.05025	0.05060
In a vacuum.....	0.05171	0.05182	0.05227

	Average.	V.P.(mm.)
In air.....	0.05039	46.2
In a vacuum.....	0.05193	47.5

A considerable amount of work was done to determine whether iodine was soluble in the vapours of a number of liquids; chiefly liquids in which iodine dissolves very readily. The method employed consisted in aspirating purified air through weighed bubblers containing the liquid under investigation. The air and vapour then passed over a tube containing iodine and maintained at 100°C. The iodine from the air-vapour mixture was absorbed in a solution of potassium iodide and estimated by titration with standardised thiosulphate solution. The air was next freed from the vapour by means of a suitable non-volatile solvent and the volume of air aspirated then measured under definite

conditions of temperature and pressure. By inserting manometers at the requisite points the pressure at various points in the system can be determined. A manometer is inserted immediately after the iodine absorbent and a second after the solvent absorbent.

Thus if

P = atmospheric pressure

P' = pressure of water vapour at the temperature of the aspirator.

p = pressure of manometer after the KI solution

$= \frac{h}{d}$ = $\frac{\text{height of mercury column}}{\text{density of mercury}}$

and p' = pressure of manometer after the solvent absorbent.

$= \frac{h'}{d'}$ = $\frac{\text{height of column of mercury}}{\text{density of mercury.}}$

Then

Pressure in the aspirator = P-(P' + p')

and Pressure at foot of iodine column= P - p

That this latter equation should be fairly accurate the tube carrying the iodine container merely passes under the surface of the potassium iodide solution and the pressure exerted there is negligible.

The heating is carried out by steam and in order that a constant temperature may always be maintained a pressure buffer, as described above, is attached to the condenser. The apparatus is shown in Figure 11

From the weight of solvent required to saturate the air, found by weighing the bubblers, the volume of the solvent under the conditions pertaining in the iodine tube was calculated by application of the gas laws. Then knowing the total quantity of iodine brought over by the mixed gases and the quantity of iodine which the air alone will bring over and which had been previously determined experimentally, the amount of iodine brought over by the solvent can be found by difference. In all these experiments the quantity of iodine which 1 litre of air is capable of carrying over at 100 °C is assumed to be constant irrespective of whether the air is pure or mixed with some other vapour.

In the first place the iodine brought over by 1 litre of air was determined. It was found that this quantity was perfectly constant and the results could be very easily reproduced. The following are the results obtained.

1 litre of air at 100 °C will bring over

(1) 0. 5123 gm. Iodine

(2) 0.5074 " "

(3) 0.512 " "

(4) 0.509 " "

The average value for 1 litre of air at 100°C is therefore 0.5099 gm. Iodine

This is the figure used in all the following experiments.

It is to be noted that this figure is in reasonable agreement with that obtained in the diffusion experiments described above. It is also in fairly good agreement with the value of 0.507 gm. Iodine obtained by Wright (J.C.S. 1915, 107, 1527.)

As a result of preliminary investigations monobrome naphthalene was found to be the best absorbent for benzene. In the following experiments with benzene this absorbent was used. Experiments were now carried out passing a definite volume of air saturated with benzene vapour over iodine heated to 100°C. Then by means of the calculation outlined above the following results for benzene were obtained.

1 litre of benzene at 100 °C brings over (1)0.3367 gm.
(2)0.3432 gm.

Though these results were rather startling, but since they are fairly concordant, they were accepted and an attempt was made to determine the effect of ethyl ether. In this experiment some peculiar phenomena were observed. After a short time of running oily drops, which persist even at 100 °C, appeared and finally the whole of the iodine fused. This definitely pointed to some interaction of the ether vapour on the surface of the iodine, possibly to give something in the nature of a solid solution. On the other hand it may have been merely a case of simple adsorption. Since iodine and benzene are definitely known to give a solid solution it was decided to verify this point. A shorter tube than usual was packed with iodine and weighed. It was placed in the heating jacket and a current of air-benzene vapour mixture aspirated over it. The loss in weight of the tube was then compared with the weight of iodine carried over and the following results were obtained.

(1) Loss in weight of tube = 0.2672 gm.

Weight of iodine carried over = 0.2589 gm.

(2) Loss in weight of tube = 0.3166 gm.

Weight of iodine carried over = 0.3148 gm.

(3) Loss in weight of tube = 0.1710 gm.

Weight of iodine carried over = 0.1706 gm.

From these results it will be seen that the loss in weight of the tube and the weight of iodine carried over are in good agreement. The fact that the loss in weight of the tube is slightly greater than the weight of iodine carried over can be easily accounted for by a slight error in the Normality Factor of the thiosulphate solution.

Further experiments were carried out on the effect of benzene vapour and the following results were obtained.

TABLE 1.

Tube (I)

Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine/litre of Benzene.
gm.	gm.	gm.	gm.
0.3322	0.3235	0.1690	0.0414
0.3353	0.3273	0.1496	0.0681
0.3374	0.3323	0.1558	0.1676
0.3500	0.3448	0.1702	0.3183
0.3400	0.3374	0.2206	0.1882

TABLE 1. contd.

Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine / litre of Benzene.
gm.	gm.	gm.	gm.
0.3534	0.3438	0.1786	0.3416
0.3502	0.3438	0.1696	0.3363
0.3454	0.3399	0.1920	0.2717
0.3484	0.3399	0.2090	0.2610
0.3450	0.3399	0.2010	0.2950
0.3482	0.3399	0.1920	0.2725
0.3404	0.3348	0.1744	0.2349
0.3444	0.3368	0.1654	0.2335
0.3460	0.3399	0.1870	0.2584
0.3572	0.3477	0.2050	0.3417
0.3436	0.3399	0.2020	0.2696

Tube (2).

Tube (3).

The above series of figures for the various tubes were obtained from consecutive runs made without interfering in any way with the iodine in the tube.

It was decided to test the effect of the concentration of the vapour passing over the iodine as that might throw some light on the irregular

nature of the results given above. In the case of the first two values obtained for benzene which were concordant, the concentrations of the vapour were totally different. This led to another series of experiments being undertaken.

As there would appear to be some surface effect it was decided to use granular fused iodine in the tubes. Table 2. gives the results of these experiments.

TABLE 2.

	Temperature of Benzene.	Concentration of Benzene in Air.	Iodine/ litre of Benzene.
	C	gm./litre	gm.
Tube (1)	17.14	0.2231	0.8802
	14.6	0.2022	0.7048
	16.25	0.2313	0.6451
	12.3	0.1792	0.5755
Tube(2)	12.0	0.1700	0.7516
	12.1	0.1771	0.4660
	11.7	0.1612	0.3161

On making a prolonged run with this second tube the iodine fused.

The effect of toluene vapour was now investigated. The absorbent used for toluene was monobrome naphthalene. The following are the results obtained.

TABLE 3.

	Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine/ litre of Toluene.
	gm.	gm.	gm.	gm.
Tube(1)		0.3325	0.0420	1.375
		0.3325	0.0475	0.8916
		0.3350	0.0510	0.6787
		0.3855	0.0435	0.4026
Tube(2)		0.3166	0.0395	0.1813
		0.3229	0.0367	0.0158
Tube(3)	0.3195	0.3166	0.0440	-0.0328
	0.3210	0.3217	0.0375	-0.6796
	0.3165	0.3204	0.0456	0.0064

Carbon Tetrachloride was the next solvent to be investigated. Again monobrome naphthalene was used as absorbent. The results are as follows.

TABLE 4.

	Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine/ litre of Carbon Tetrachloride.
	gm.	gm.	gm.	gm.
Tube (1)	0.3285	0.3356	0.2565	0.2319
	0.3440	0.3462	0.2858	0.4498
	0.3368	0.3458	0.2890	0.3571
	0.3355	0.3482	0.2710	0.4239
	0.3392	0.3458	0.2905	0.3416
	0.3340	0.3445	0.2730	0.3503
Tube (2)	0.3560	0.3533	0.2980	0.4218
	0.3445	0.3420	0.2965	0.3088
	0.3492	0.3477	0.2835	0.4274
	0.3424	0.3407	0.3170	0.3344

The results obtained using Chloroform are given in Table 5. The absorbent used was monobrome naphthalene.

TABLE 5.

	Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine / litre of Chloroform.
	gm.	gm.	gm.	gm.
Tube (1)	0.3639	0.3623	0.3610	0.4602
	0.3795	0.3799	0.3560	0.5601
	0.3665	0.3660	0.4000	0.4370
Tube (2)	0.3726	0.3711	0.3755	0.4819
	0.3664	0.3638	0.3685	0.5000
	0.3638	0.3648	0.3730	0.4200
	0.3738	0.3774	0.3820	0.5435
	0.3740	0.3749	0.3820	0.5366

Dichlor Ethylene was next investigated and was absorbed in monobrome naphthalene.

TABLE 6.

	Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine / litre of Dichlor Ethylene.
	gm.	gm.	gm.	gm.
Tube (1)	0.4250	0.4268	0.5800	0.5374
	0.3880	0.3888	0.4345	0.4777
	0.4000	0.4102	0.5818	0.4804
	0.3950	0.4008	0.5050	0.4729
	0.3850	0.3942	0.4580	0.4889
Tube (2)	0.3890	0.3942	0.4140	0.5658
	0.3960	0.4023	0.4742	0.5157
	0.3715	0.3768	0.4310	0.4109
	0.3895	0.3956	0.4950	0.4466

The action of ethyl ether vapour was now investigated. A bubbler of water followed by another containing sulphuric acid was found to be an effective absorbent. A single run gave the following result.

1 Litre of Ether vapour at 100°C carries over

0.227 gm. Iodine.

During this experiment oily drops separated in the iodine tube and on attempting to make a second run the whole mass of iodine fused. In order to decrease the quantity of ether vapour in the air mixture the bubblers containing the ether were immersed in ice during the experiments.

TABLE 7.

Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine / litre of Ether.
gm.	gm.	gm.	gm.
0.4204	0.4179	0.5206	0.4189
0.4222	0.4140	0.5440	0.4056
0.4190	0.4001	0.5130	0.3830
0.4034	0.3900	0.5000	0.3292

As the quantity of ether in the mixture was considered still to be too great, a solution of ether in liquid paraffin was made; 2 parts of ether to 5 parts of liquid paraffin. This mixture was kept in ice during the experiments. To prevent the quantity of ether vapour in the air mixture during any experiment becoming too small, a quantity of ether was added to the paraffin solution after

each run so that the volume of ether-paraffin solution should always be the same at the beginning of each run.

TABLE 8.

	Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine / litre of Ether.
	gm.	gm.	gm.	gm.
Tube (1)	0.3836	0.3799	0.3010	0.4850
	0.3798	0.3783	0.2740	0.5161
	0.3652	0.3647	0.2774	0.4205
	0.3858	0.3850	0.2978	0.5178
Tube (2)	0.3760	0.3761	0.3540	0.3956
	0.3825	0.3758	0.4446	0.2902
	0.3730	0.3748	0.3680	0.3576
	0.3850	0.3874	0.3432	0.4680
	0.2654	0.2634	0.2676	0.1887
Tube (3)	0.3876	0.3836	0.3650	0.4128
	0.3950	0.3951	0.3520	0.4821
	0.3770	0.3748	0.3072	0.3818
	0.3634	0.3634	0.2778	0.3691
	0.3556	0.3583	0.2976	0.3331

The next solvent to be investigated was ethyl alcohol. In this case a bubbler of water followed by one of sulphuric acid was found to be an effective absorbent.

TABLE 9.

	Weight of iodine carried over.	Weight of solvent used.	Iodine / litre of Alcohol.
	gm.	gm.	gm.
Tube (1)	0.3375	0.0507	0.4506
	0.3413	0.0270	0.7806
Tube (2)	0.3464	0.0310	0.9780
	0.3439	0.0400	0.5803
	0.3401	0.0315	0.7281
	0.3451	0.0365	0.8218
	0.3464	0.0365	0.9800
	0.3464	0.0340	0.8949

As these results were so erratic it was decided to pass a current of pure air over the iodine between each run using the air-alcohol mixture to see if any value approaching constant could be obtained. Thus approximately one and a half

litres of air were passed over the iodine between each of the determinations shown in the following table.

TABLE 10.

Weight of iodine carried over.	Weight of solvent used	Iodine / litre of Alcohol.
gm.	gm.	gm.
0.3274	0.0290	-0.0061
0.3274	0.0320	0.0000
0.3223	0.0360	-0.0013

Whereas in all the above experiments the time of running the mixture over the iodine was absolutely constant for each solvent, it was decided to try the effect of varying the time in the case of alcohol. The following results were obtained.

Time of experiment.....1 hour.

1litre of alcohol at 100°C brings over

(1) 0.3263 gm. Iodine.

(2) 0.3218 " "

Time of experiment....1/2 hour.

1 litre of alcohol at 100°C brings over

(1) 0.6078 gm. Iodine.

(2) 0.6324 " "

The next solvent investigated was water. In this case no absorbent was required.

TABLE 11.

	Loss in weight of tube.	Weight of iodine carried over.	Weight of solvent used.	Iodine / litre of Water.
	gm.	gm.	gm.	gm.
Tube (1).	0.3440	0.3348	0.0130	0.6376
Tube (2).	0.3142	0.3097	0.0102	-0.3361
	0.3170	0.3097	0.0114	-0.2386
	0.3240	0.3185	0.0104	-0.1732
	0.3140	0.3097	0.0140	-0.1953
	0.3130	0.3097	0.0132	-0.0967
	0.3256	0.3210	0.0096	0.2838
	0.3268	0.3222	0.0104	0.1552
	0.3036	0.3041	0.0080	-0.9813
	0.3276	0.2846	0.0080	-2.813
	0.3248	0.3185	0.0082	-0.2631
Tube (3).	0.3330	0.3270	0.0086	0.3667
	0.3250	0.3185	0.0074	-0.4349
	0.3216	0.3172	0.0056	-0.6717
	0.3274	0.3270	0.0060	-0.3916
	0.3106	0.3047	0.0086	-1.335

The effect of carbon dioxide on iodine was next considered. The use of carbon dioxide generated from solid sodium carbonate by means of sulphuric acid was tried but it was found that it was impossible to use this method owing to the very great fluctuations in pressure of the carbon dioxide. By using a solution of the carbonate and carefully adding the acid these fluctuations were more or less avoided. In this manner the pressure variations were reduced to about 2 mm. of mercury. The air-carbon dioxide mixture was carefully dried before passing over the iodine and the carbon dioxide was then absorbed in a mixture of soda lime and stick caustic potash. This absorbent was followed by a small lime water indicator. The results with carbon dioxide are as follows.

TABLE 12.

Weight of iodine carried over.	Volume of Carbon Dioxide used.	Iodine / litre of Carbon Dioxide.
gm.	litre.	gm.
0.2905	0.1955	-0.1836
0.3238	0.0879	-0.3609
0.3520	0.1689	0.1848
0.3391	0.0870	0.2392
0.3687	0.1972	0.2454
0.3520	0.1262	0.2504
0.3481	0.1115	0.2151

It was found that if a current of air is aspirated over ammonium carbonate maintained at 100°C a considerable quantity of carbon dioxide is carried over. This method was utilised to give a steady supply of carbon dioxide under non-fluctuating pressure conditions. The air after passing over the ammonium carbonate was purified from ammonia and water by passing first through dilute sulphuric acid and then through concentrated sulphuric acid. The absorbent for the carbon dioxide was again a mixture of soda lime and stick caustic potash, and also followed by a lime water indicator.

TABLE 13.

Weight of iodine carried over.	Weight of Carbon Dioxide used.	Iodine / litre of Carbon Dioxide.
gm.	gm.	gm.
0.4723	0.6958	0.2973
0.4032	0.3685	0.3054
0.4199	0.5485	0.3318

In several of the foregoing tables of results the amount of iodine carried over per litre of solvent vapour is given as being a negative quantity. Since the assumption has been made at the beginning of this work that air whether pure or mixed with some vapour will always carry over the same quantity of iodine the negative sign merely indicates that the total quantity of iodine brought over by the mixture is less than air would bring over if aspirated alone. Thus in the case of the first result in Table 12.

If 1 litre of air brings over 0.5099 gm. Iodine
Then 1 litre of air plus 1 litre of carbon dioxide
will bring over 0.5099 - 0.1836
= 0.3236 gm. Iodine.

An entirely different type of experiment based on measuring the change in pressure when two equal volumes of gas are mixed was undertaken. The apparatus consisted of a large U-tube the limbs of which were fitted with well ground cocks and were

marked so that the volume in each limb above the mark was equal. This U-tube was connected to a manometer tube by means of a connection sealed in the bottom of the tube. It was suspended in a large inverted jar acting as an air thermostat. The levelling manometer tube was mounted on a scale.

The technique of the experiment consisted in filling one limb of the tube to the mark on the limb with a gas at atmospheric pressure. The other limb is then filled with the other gas under investigation also under atmospheric pressure. Thus there are two volumes of gases equal under the same conditions of temperature and pressure. The atmospheric temperature and pressure are noted, the taps closed and the height of the levelling manometer tube on the scale noted. The levelling tube is then lowered until the mercury drops below the bend of the U-tube and so allows the two gases to come in contact. After allowing the gases to diffuse the levelling tube is raised until the volume in the limbs is equal to the original volumes. The atmospheric temperature and pressure and the height on the scale of the levelling tube are noted. The value of P/T is then calculated for the gases before and after mixing, where

P = total pressure on the gas

and T = absolute temperature of the gas.

TABLE 14.

Ammonia and Dry Air.

Atmospheric Temperature. °C	Atmospheric Pressure. mm.	Scale Reading. cm.	P/T
18.1	759.6	2.2	2.609
17.5	760.0	2.0	2.617
14.2	755.5	2.1	2.630
15.2	755.6	2.8	2.620
15.9	755.7	2.1	2.617
16.7	755.7	2.7	2.606
18.1	755.7	2.1	2.596
18.5	755.2	2.2	2.590
18.7	754.7	2.1	2.587
18.8	755.2	2.7	2.586

TABLE 15.

Ammonia and Air saturated with water at 15°C

Atmospheric Temperature. °C	Atmospheric Pressure. mm.	Scale Reading. cm.	P/T
17.6	752.0	2.1	2.587
17.8	752.3	2.5	2.585
18.2	752.3	2.1	2.583
18.0	752.3	2.6	2.58

TABLE 16.

Ammonia and Ethyl Alcohol.

Atmospheric Temperature. °C	Atmospheric Pressure. mm.	Scale Reading. cm.	P/T
17.4	762.5	2.0	2.626
17.3	763.2	2.0	2.629
17.5	763.9	2.0	2.630
17.7	764.2	2.2	2.622
18.0	764.3	2.0	2.627
17.9	764.9	2.8	2.602
17.9	772.4	2.0	2.656
17.5	773.0	2.8	2.632

TABLE 17.

Ammonia and Methyl Alcohol.

Atmospheric Temperature. °C	Atmospheric Pressure. mm.	Scale Reading. cm.	P/T
14.1	728.0	2.2	2.535
15.2	727.8	2.9	2.501
15.5	726.8	2.1	2.519
15.9	726.3	2.8	2.489

TABLE 18.

Ethyl Alcohol and Methyl Alcohol.

Atmospheric Temperature. °C	Atmospheric Pressure. mm.	Scale Reading. cm.	P/T
19.8	754.0	1.8	2.575
19.5	754.5	2.4	2.560
19.9	755.0	1.9	2.524
15.2	741.6	1.9	2.577
15.2	741.7	1.8	2.573
19.8	739.2	2.5	2.500
20.5	739.2	2.0	2.518
15.5	736.8	0.9	2.592
16.1	737.0	2.0	2.549
18.2	738.2	2.7	2.510
18.8	738.6	2.2	2.532
13.7	745.6	0.4	2.663
14.2	745.5	2.1	2.596
15.4	739.7	3.7	2.509

In the foregoing experiments the vapours of ethyl and methyl alcohols were obtained by saturating air with the vapour at atmospheric temperature.

As the diffusion of the gases is very slow the time required to carry out each of these experiments is excessive. Thus a new type of apparatus was evolved.

In this case the method consists in measuring the actual volume obtained on mixing two known volumes of gases. The mixing is done mechanically and not by diffusion and so the time of the experiment is very considerably reduced. The apparatus consisted of two eudiometer tubes connected together. One of these tubes had a large bulb at the top of the tube. A definite volume of gas was carefully measured out in one tube and then transferred to the bulb in the other. A known volume of the second gas was then passed over into the bulb. By repeatedly and rapidly altering the pressure on the gases in the bulb mechanical mixing was obtained. The mixed gases were then transferred back to the measuring tube and their volume measured under the same conditions as the individual gases were measured.

The following results have been obtained.

TABLE 19.

Sulphur Dioxide and Air.

Volume of Sulphur Dioxide. c.c.	Volume of Air. c.c.	Volume of Mixture. c.c.
25.0	25.0	50.4
25.0	25.0	50.2
25.0	25.0	50.2
25.0	25.0	50.2
25.0	25.0	50.2
25.0	25.0	50.3
25.0	25.0	50.3
25.0	25.0	50.3
25.0	25.0	50.3
Av. 25.0	25.0	50.27

TABLE 20.

Sulphur Dioxide and Ethyl Alcohol.

Volume of Sulphur Dioxide. c.c.	Volume of Ethyl Alcohol. c.c.	Volume of Mixture. c.c.
25.0	25.0	50.3
25.0	25.0	50.2
25.0	25.0	50.4
25.0	25.0	50.3
Av. 25.0	25.0	50.3

TABLE 21.

Sulphur Dioxide and Methyl Alcohol.

Volume of Sulphur Dioxide.	Volume of Methyl Alcohol.	Volume of Mixture.
c.c. 25.0	c.c. 25.0	c.c. 50.2

TABLE 22

Sulphur Dioxide and Water Vapour.

Volume of Sulphur Dioxide.	Volume of Water Vapour.	Volume of Mixture.
c.c. 25.0	c.c. 25.0	c.c. 50.0
25.0	25.0	50.2
25.0	25.0	50.2
25.0	25.0	50.0
25.0	25.0	50.0
25.0	25.0	50.0
25.0	25.0	50.0
25.0	25.0	49.9
25.0	25.0	50.1
25.0	25.0	50.1
25.0	25.0	50.2
25.0	25.0	50.1
Av.25.0	25.0	50.07

TABLE 23.

Carbon Dioxide and Air.

Volume of Carbon Dioxide.	Volume of Air.	Volume of Mixture.
c.c.	c.c.	c.c.
25.0	25.0	50.1
25.0	25.0	50.2
25.0	25.0	50.2
25.0	25.0	50.3
25.0	25.0	50.2
Av.25.0	25.0	50.2

TABLE 24.

Carbon Dioxide and Water Vapour.

Volume of Carbon Dioxide.	Volume of Water Vapour.	Volume of Mixture.
c.c.	c.c.	c.c.
25.0	25.0	50.1
25.0	25.0	50.1
25.0	25.0	50.1
25.0	25.0	50.0
25.0	25.0	50.1
25.0	25.0	50.0
25.0	25.0	50.0
25.0	25.0	50.0
25.0	25.0	50.0
Av.25.0	25.0	50.03

TABLE 25.

Carbon Dioxide and Ethyl Alcohol.

Volume of Carbon Dioxide.	Volume of Ethyl Alcohol.	Volume of Mixture.
c.c.	c.c.	c.c.
25.0	25.0	50.2
25.0	25.0	50.2
25.0	25.0	50.2
25.0	25.0	50.6
25.0	25.0	50.2
25.0	25.0	50.3
Av.25.0	25.0	50.28

TABLE 26.

Carbon Dioxide and Methyl Alcohol.

Volume of Carbon Dioxide.	Volume of Methyl Alcohol.	Volume of Mixture.
c.c.	c.c.	c.c.
25.0	25.0	50.2
25.0	25.0	50.2
25.0	25.0	50.4
25.0	25.0	50.4
25.0	25.0	50.3
Av.25.0	25.0	50.3

In the above experiments, as in the diffusion experiments, the vapours of ethyl and methyl alcohols and water were obtained by saturating air with the vapour at atmospheric temperature.

CONSIDERATION OF RESULTS.

Nernst (Theoretical Chem. 1911, 56.) has stated that " if we bring a simple liquid into a vacuum, evaporation takes place till the pressure of the gas formed has reached a definite maximal value, namely, the corresponding vapour pressure. In presence of another, but an indifferent gas, evaporation takes place until the partial pressure of the resulting vapour is equal to the vapour pressure." It does not appear to be generally recognised that this statement is an inexact assumption; that this is so however, is shown by the determination of the vapour pressure of iodine in presence of air and in a vacuum as is described above. There it is found that the vapour pressure of iodine in a vacuum is approximately 2.8% greater than the vapour pressure in presence of air. That the vapour pressure of a liquid is lower in presence

of an inert gas is also borne out by the work of Regnault, (Ann. Chim. Phys. 1845, 15, 129.); of Campbell, (Trans. Far. Soc. 1914-15, Vol. 10, 197.) and of Sayce and Briscoe, (J.C.S. 1929, 1302.) Thus it follows that the concentration of a saturated vapour is not a true measure of the vapour pressure of a gas, and therefore that the very large number of vapour pressure measurements which have been made by the gas saturation method are inaccurate and are subject to an error unknown in extent but which may be very appreciable. This also disproves the suggestion put forward by Dewar to explain the difference in colour of the vapour of iodine when in a vacuum and when in the presence of air.

From a consideration of the spectra of iodine in vacuum and in presence of another gas it follows from the widening and displacement of the absorption band that the iodine is being affected in some manner. Again under the conditions of the experiment this cannot be due to any increase or decrease in volatility in presence of the inert gas. However since all the gases investigated have given absolutely identical results it follows that it cannot be due to any form of chemical interaction taking place. Also it would appear to be equally

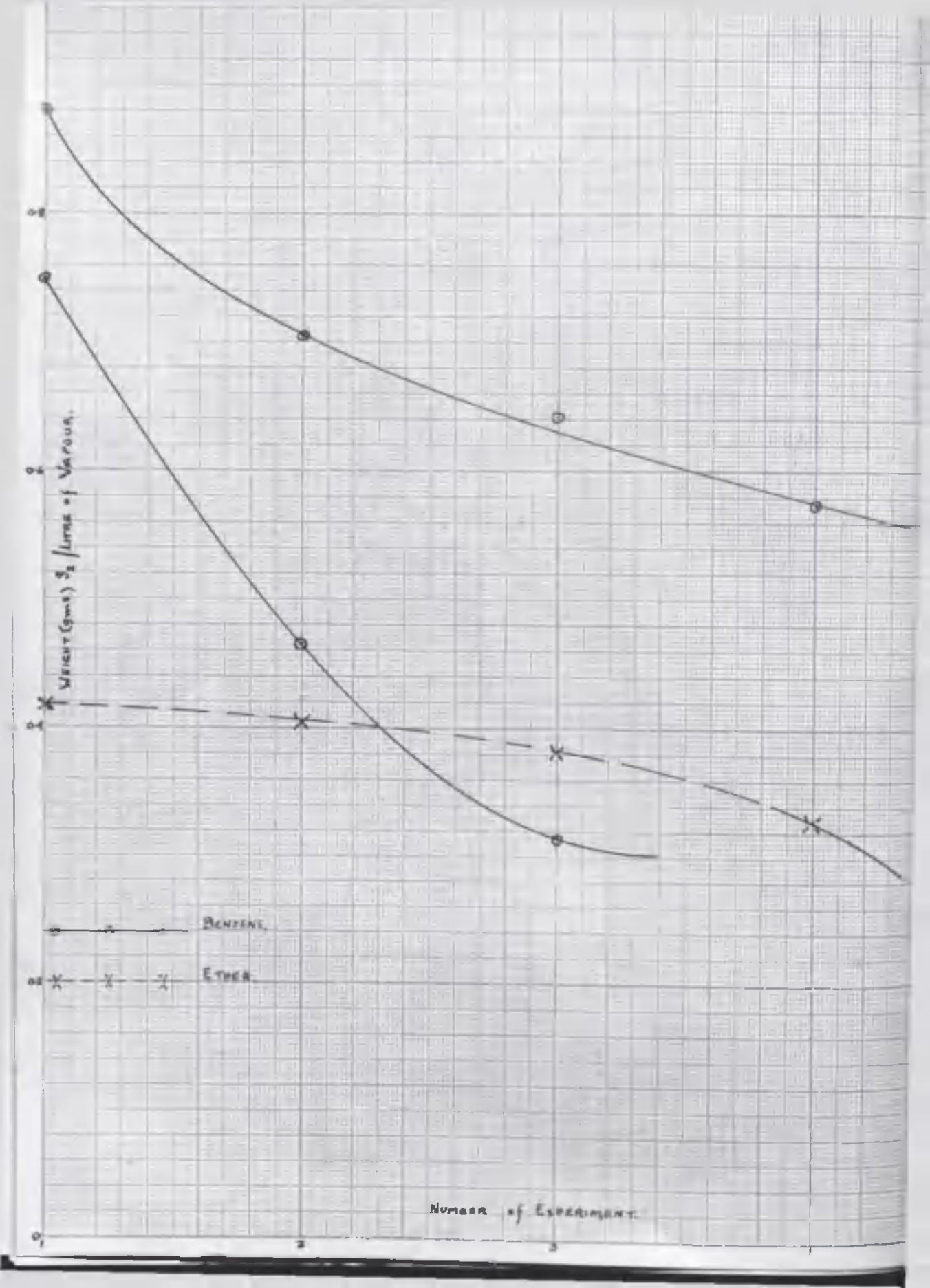
improbable that there is any solubility of the iodine in the various gases. The most probable explanation of this widening and displacement of the absorption band would appear to lie in some pressure effect on the iodine vapour. Under the conditions of the experiment the pressure exerted by the various gases would be almost identical.

The results obtained by aspirating a current of vapour saturated air over a column of iodine are very irregular but it would appear to be possible to give an explanation of this. In the first place since most of the solvents investigated, the exceptions being carbon tetrachlodide, water and carbon dioxide, can bring over quantities of iodine considerably greater than that carried over by air it would appear that solubility of the iodine is actually taking place in the solvent vapour. In all probability carbon tetrachloride is also a solvent in the vapour phase though no large quantity of iodine was brought over. The incidence of this large value, in a large number of cases the first value to be determined with a new tube, is strictly analogous to the increase in vapour pressure of water when first brought in contact with ammonia, as was found by Perman (J.C.S. 1903, 83, 1168.)

In this work Perman found that after this increase, the vapour pressure of the water gradually fell off due to the solution of the ammonia in the liquid water. But the presence of these high values would definitely seem to point to solution in the vapour phase.

The extreme irregularity of the results is undoubtedly due to adsorption of the solvent vapour on the surface of the iodine. Since the surface of the iodine cannot be controlled it will be impossible to obtain reproducible results. Thus the degree of adsorption, and so the corresponding decrease in the vapour pressure of the iodine, determines the amount of iodine carried over by the vapour. Generally speaking it has been found that there is no difference between the loss in weight of the iodine tube and the weight of iodine carried over to bear out this theory of adsorption. However though no general indication can be given in some cases there are definite indications by comparing these weights that adsorption does take place; (cf. Table 3, (3), and Table 4, (1).)

With benzene it would appear to be possible to obtain comparable results or rather series of results. The type of result in this case


Weight (gms.) S_2 / Litre of Vapour.
Benzene.
Ether.
Number of Experiment.
1
2
3

shows a gradual falling off in the amount of iodine carried over, as si shown in the accompanying graph. Thus we are no longer obtaining a surface effect but are definitely forming a solid solution. It is known that benzene and iodine do definitely form a solid solution. This would appear to be existing even at 100°C. With this solvent we obtain a high initial value indicating solubility in the vapour before the formation of the solid solution begins. Ether gives one set of results (Table 7) which gives a very definite curve as is shown opposite. This would also tend to the idea of the formation of a solid solution. The fact that the other series are quite irregular is probably due to the fact that the additive compound formed, as is very strongly indicated by the separation of oily drops throughout the iodine tube, dissolves some of the ether vapour and the resultant vapour pressure changes completely mask the regularly diminishing vapour pressure of the iodine. No trace of any additive compound of iodine and ether can be found in literature though the corresponding additive compounds with Bromine (Schutzenberger, Liebig Ann. 167, 86.) and with Hydrogen Iodide (Messiger and Engels, Ber. 1863, 21, 327.) are known. However the formation of these oily drops

which persist even at 100°C, is exceedingly marked and the ease with which it is possible to liquefy the whole of the iodine mass definitely support the idea of solid solution formation. A series of gradually decreasing results was also obtained when using toluene but most probably this is misleading and merely the result of chance.

Further indications of the solubility of iodine in a vapour are afforded when using alcohol vapour. As is shown above the time factor appears to play an important part. It seems that in this case the amount of iodine carried over varies inversely as the time of the experiment. This can be explained if solution takes place with the subsequent dissociation of the dissolved iodine in the alcohol vapour.

The results given in Table 11. indicate that the concentration of the solvent vapour passing over the iodine has no definite influence and that the solubility in the vapour phase is not proportional to the concentration of the solvent vapour.

At present the results obtained with water are quite inexplicable though probably

there is no case of solution in the vapour. In the case of carbon dioxide there would also appear to be no indication of solution. The fact that the quantity of iodine carried over is less than that carried over by air and that the results are irregular would indicate again that in presence of another atmosphere vapour pressure is lowered and also that there is a certain amount of adsorption of the carbon dioxide by the iodine.

In the case of the mixing of gases either by diffusion or by mechanical means there are very definite indications that the same effect does not take place in the case of all gas mixtures. In considering the results of the diffusion experiments as shown in Tables 14, 16, 17 and 18 it is obvious that the value of P/T is considerably different before and after mixing the gases, whereas in Table 15 the values are identical. This change in the value of P/T indicates that if two equal volumes of gas be mixed and the resultant volume measured under exactly the same conditions of temperature and pressure as the original volumes then the resultant mixture does not have a volume equal to twice the volume of either of the constituents. In the other case where the value of P/T is the same before

and after mixing then the resultant volume is equal to twice the volume of either constituent. The same type of result is also obtained on actually measuring the resultant volume obtained by mixing two equal volumes of gases. In some cases the resultant volume is equal to twice and in others to something greater than twice the original volume. In the larger number of gases examined it is found that the resultant mixture has a volume greater than twice the original volume. Since the gases and vapours investigated do not obey Boyles' Law it follows that on simple mixing the resultant volume should be greater than twice the original volume. Thus it follows that in the above cases simple mixing takes place. However in certain cases; ammonia and water vapour, sulphur dioxide and water vapour and carbon dioxide and water vapour; (Tables 15, 22 and 24) some further effect is taking place. Since these gases do not obey Boyles' Law and since the resultant volume is exactly twice the original volume, it follows that simple mixing no longer takes place. There is undoubtedly some form of interaction and the most feasible explanation of the above phenomenon is that the gases are mutually soluble.

CONCLUSIONS.

1st. Solubility in the vapour phase must be considered as a definite property of definite vapours with regard to some particular substances; but not as a general property of all gases and vapours with regard to all substances.

2nd. The vapour pressure of a substance is lowered by the presence of an inert or indifferent atmosphere.

3rd. Arising from the above conclusions the current saturation method of determining vapour pressures does not give accurate results.

4th. Solid solutions can definitely be formed between solids and vapours.